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Hybrid multi-porphyrin supramolecular assemblies: Synthesis and structure elucidation by 2D DOSY NMR studies

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ABSTRACT

Design and synthesis of hybrid multi-metalloporphyrin assembles have been performed. The chemical structure of the synthesized complexes and their stability in solution were confirmed by the methods of 2D DOSY NMR spectroscopy, which have been specially adapted for these supramolecular architectures in solutions.

Tin(IV)-porphyrins are ideal scaffolds for the construction of axially bonded multi-porphyrin supramolecular assemblies. In the literature there are described multi-porphyrin arrays, in which porphyrin moieties of different nature are axially coordinated from both sides of the tin(IV)-porphyrin core [1–8] and multi-porphyrin supramolecular assemblies in which the porphyrin macrocycles are linked to the tin(IV)-porphyrin through polyfunctional organic ligands [9–12].

In continuation of our studies in the field of supramolecular chemistry of porphyrins [7,8,13–19], in this work synthesis and NMR studies of Ru(II) tetraphenylporphyrin [RuP(CO) (I)] and complexes of I and Sn(IV)porphyrin [$SnP(OH)_2$ (II)] with 3-hydroxypyridine [L] with one $SnP(L)_2$ (III)] and two [$SnP(OH)_2$-4RuP(CO) (IV), $SnP(L)_2$-6RuP(CO) (V)] centers of binding were carried out. Complexes (IV) and (V) were investigated by 2D NMR spectroscopy.

It was found that due to peculiarities of the chemical structure and to the low concentration of the complex in solution studies by 1H NMR, 2D 1H-1H ROESY, 2D 1H-1H COSY for this system are not sufficiently informative. In addition, the interpretation of results is complicated by the fact that NMR signals in the spectra of the molecules at the same time depend on two factors: a change in the shielding and a variation of the electron density distribution upon complex formation. Thus questions about the size and stability of the complexes formed remains open. Therefore, to obtain direct evidence of the fact of complex formation and information about their size, other approaches should be used.

We have applied an approach to elucidate the structures for complex that is based on the analysis of two-dimensional diffusion high-resolution spectroscopy (2D DOSY).

1. Experimental

1.1. Preparation of Ru(II)-[5,10,15,20-tetrakis(phenyl)porphyrin]

[$RuP(CO)(H_2O)$, I, Fig. 1] was obtained from 5,10,15,20-tetrakis(phenyl)porphyrin according with [6]. R_f = 0.67 (eluent: chloroform). UV–Vis (benzene, nm): λ_{max} (log ε) 411 (5.21), 490 (3.66), 529 (4.30). IR (KBr, cm^{-1}): ν_{CO} 1948. FAB Mass Spectrum: [m/z (rel. intens. %)]: 743.5 (79) (calc. 742.4). Anal. Calcd. for $C_{45}H_{32}N_4O_2Ru$: C, 66.09; H,3.92; N, 6.85. Found: C, 66.01; H, 3.89; N, 6.81.

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